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SYNTHESIS OF CYCLIC ETHERS

BY

HERMAN ALFRED GOLDSTEIN

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

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DEGREE OF BACHELOR OF SCIENCE

R. E. Rindfusz

Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF Chemistry

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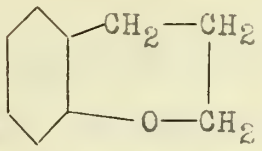
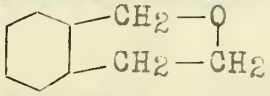
H.A.Goldstien

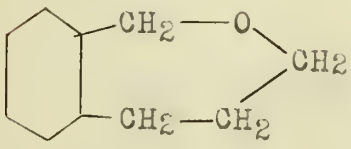
THE SYNTHESIS OF CYLIC ETHERS

INTRODUCTION

Although chromane  has been known for a number of years, as have also a number of other types of cylic ethers, its isomer  has never been prepared. With the exception of one cylic ether, phthalan (1) no other benzo cylic ethers with the oxygen removed from the ring have ever been synthesized.

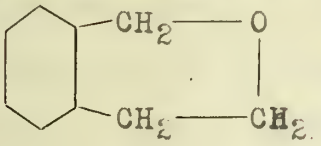
The object of this research was to prepare such a compound and its homologue.

In the preparation of chromane by the old methods, the complexity of the substances used made it a difficult problem. Recently, however, Rindfusz (2) has prepared chromane very easily by treating phenol with trimethylene chlorhydrin and zinc chloride. In this work, the method of Rindfusz has been applied to the preparation of iso-chromane and its homologue, 2,3-benzo-trimethylene oxide,

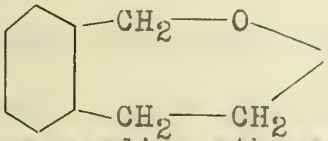


THEORETICAL

By starting with benzyl alcohol in place of phenol we are thereby able to move the oxygen out one place further along the chain. In the synthesis of isochromane,

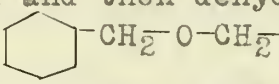


and 2,3-benzo-trimethylene oxide,

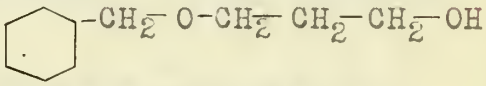


, the homologue of isochromane, the corresponding ethers were first prepared and then dehydrated.

Beta hydroxy ethyl benzyl ether

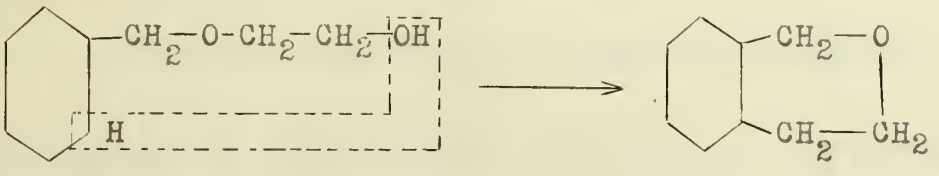


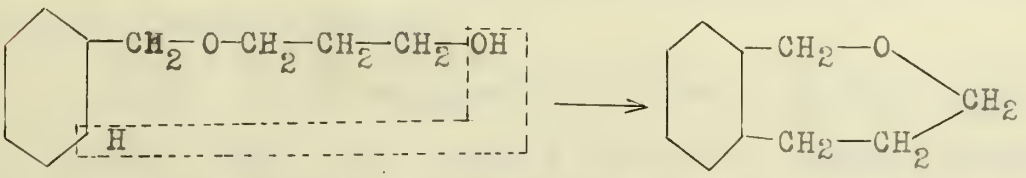
and γ - hydroxy propyl benzyl ether



were synthesized by treating sodium benzylate with the corresponding chlorhydrin.

By dehydration of these ethers, isochromane and its homologue have been prepared.

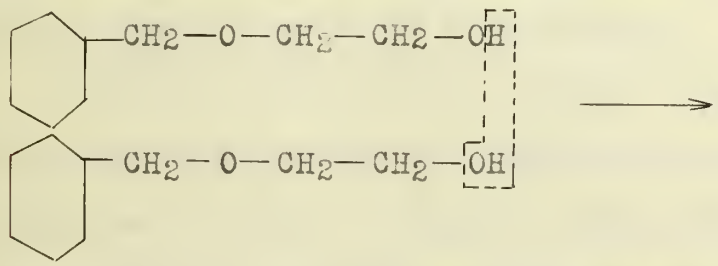


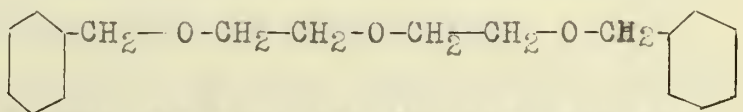


The dehydrating agents used were $ZnCl_2$ and P_2O_5. The results obtained indicated that the use of P_2O_5 is more satisfactory.

The results obtained varied from 30 to 45% of the theoretical. In a few cases, yields between 60 and 70% were obtained.

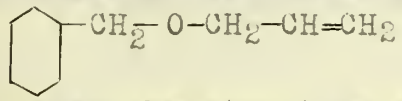
The mechanism of this dehydration was expected to produce cyclic ethers only. However, in each case, the reaction seemed to go in two directions. First, in the case of isochromane a product was obtained which proved to be a solid and liquid mixture. The solid upon extraction with ethyl alcohol and crystallization from water gave a pure substance with a definite melting point of 121° C. The liquid, by analysis, was isochromane. The proportion of the solid obtained to liquid was very small. On several occasions of preparation, the solid was absent entirely. The formation of this solid compound leads to the belief that it is the dehydration product of two molecules of beta hydroxy ethyl benzyl ether.



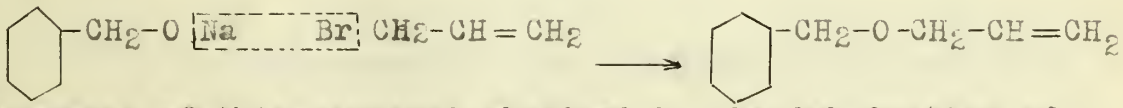


Not enough of this compound was obtained for analysis and positive identification.

Second, in the dehydration of the γ -hydroxy propyl benzyl ether, there also appeared to be two products formed.

In this case, both compounds were liquids with only a variation in boiling points. They were separated by fractional distillation. Here, however, the dehydration went in another direction. The tendency was to produce an unsaturated, straight chain ether,  , along with the closed ring ether. From the structure of the compound, it can plainly be seen that the chain attached to the oxygen is the allyl group.

The next step taken was to prepare such an ether. This was very easily accomplished by treating sodium benzylate with allyl bromide.



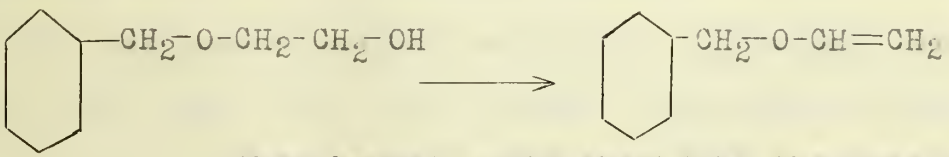
The amount of this compound obtained by the dehydration of the hydroxy propyl benzyl ether was only a small fraction of the quantity used for dehydration.

However, since the main product does not correspond to the benzyl allyl ether so prepared, the dehydration must have taken place to give the cyclic ether. Thus the structure of the 2,3-benzo-trimethylene oxide is established.

In studying the action of Br_2 and $KMnO_4$ on the various ethers, additional proof of their structure was obtained. Thus, the 2,3-benzo-trimethylene oxide decolorizes Br_2 very rapidly, giving off large volumes of HBr. The allyl benzyl ether decolorizes more slowly without any evolution of HBr.

$KMnO_4$ is decolorized by the allyl benzyl ether but not as rapidly as by the 2,3-benzo-trimethylene oxide.

Isochromane decolorizes Br_2 slowly giving off HBr upon warming. The oxidation of isochromane by $KMnO_4$ in alkaline solution to phthalic acid was attempted in order to prove its structure. If the dehydration went as supposed and yielded the isochromane, then oxidation should phthalic acid. On the other hand, if the oxidation took place to give an ethylene compound, vinyl benzyl ether.

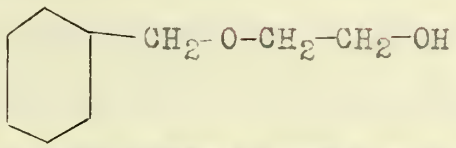


then benzoic acid should be the product of oxidation. On the addition of $KMnO_4$, rapid action took place, but no product of oxidation could be isolated. Consequently, there is no direct and absolute proof that isochromane is formed. However, since it has been definitely shown that 2,3-benzo-trimethylene oxide forms by the same reaction, even though the ring which is closed contains seven members, there can be practically no doubt that the action takes the same course to yield the analagous six membered ring.

These reactions might possibly work with other types of cyclic ethers in which the oxygen could be moved out one more place along the chain.

EXPERIMENTAL

Beta hydroxy ethyl benzyl ether



46 grams of metallic sodium were added at room temperature to 650 c.c. of benzyl alcohol in a two liter flask with a reflux condenser. The reaction takes place with the evolution of considerable heat. After all the sodium was dissolved, 180 c.c. of ethylene chlorhydrin were added to the cold solution of sodium benzylate. On heating the flask with a free flame for a few minutes, the solution turned to a reddish brown color. Refluxed for 5 hours. The solution after refluxing is of a pale yellow color. On standing for a little while, the sodium salt settles out leaving a clear solution. Poured off as much as possible of the clear solution and filtered the remaining salt solution by suction. The salt is in a semi-colloidal condition which makes filtration difficult. The precipitate is washed with a little benzyl alcohol or ethyl ether.

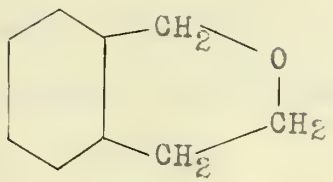
The solution is then distilled under diminished pressure with a vacuum of 30 mm. or less because the ether starts to decompose under a smaller vacuum, The benzyl alcohol begins to distill over at 110°C. at about 20 mm. After all the unchanged alcohol is distilled over, the temperature rises very rapidly to about 170 degrees.

The beta hydroxy ethyl benzyl ether distills over at a constant temperature of 165 degrees at 20mm. The range of temperature at which the ether was collected varied from 176 to 188 degrees. The ether is golden yellow in color and has a specific gravity of 1.05835 at 26° C. It has an index of refraction of 1.5245. It is insoluble in water and alcohol but soluble in ethyl ether. The yields obtained vary from 30 to 35% of the theoretical. The small yield is due to the formation of higher boiling compounds which cannot be collected as they decompose at this pressure.

Substance; 0.1208 gm. : CO_2, 0.3138 gm. : H_2O, 0.0824gm.

Calc. for $C_9H_{12}O_2$	Found
C = 71.05%	C = 70.84%
H = 7.89%	H = 7.62%

Isochromane



This compound is prepared from beta hydroxy ethyl benzyl ether by dehydration, either with zinc chloride or phosphorus pentoxide. Dehydration with P_2O_5 in toluene solution gives better results and is time-saving.

10 grams of beta hydroxy ethyl benzyl ether are dissolved in about 200 c.c. of toluene to which is added 12 grams of anhydrous P_2O_5 . The mixture is heated for an hour in a 500 c.c. flask connected with a reflux condenser. The toluene solution containing the isochromane is poured off into a Claisson distilling bulb and the toluene distilled off. As the temperature rises a smaller flask is put in place of the one containing the distilled toluene to collect the isochromane. With a pressure of 20 mm., yellow drops begin to come over at 125 degrees. The temperature remains constant at 140° while most of the substance comes over. The temperature ranged from 138 to 148 degrees at 23 mm. The distillate solidified into a yellow mass.

The distillate contains the two dehydrated products. The solid substance is extracted with ethyl alcohol, evaporated down and crystallized from water. The solid is white. The extracted liquid is the isochromane. It is a clear yellow oil.

25 to 35% yields are obtained.

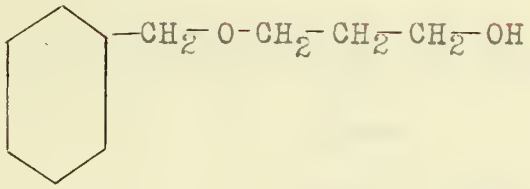
Specific gravity 1.0122 at 26° C

Index of refraction 1.5645

Substance, 0.1276 gm. ; CO_2, 0.3747 gm. ; H_2O, 0.0880 gm.

Calc. for $C_9H_{10}O$	Found
C = 80.6%	C = 80.31%
H = 7.46%	H = 7.72%

γ - hydroxy propyl benzyl ether



This compound is prepared by treating the sodium derivative of benzyl alcohol with trimethylene chlorhydrin. The method of preparation is analagous to the preparation of the beta hydroxy ethyl benzyl ether.

Metallic sodium is dissolved in benzyl alcohol at room temperature. After all the sodium is dissolved, trimethylene chlorhydrin is added in the proportion of 1 to 3, based on the benzyl alcohol used, and the mixture is refluxed for 4 hours. On standing, the sodium chloride settles out and the solutio is filtered under suction. The benzyl alcohol solution is distilled under dimished pressure. After all the alcohol is distilled off, the γ -hydroxy propyl benzyl ether begins to come over at 185° C. at a pressure of 21 mm. The boiling point remains constant at 198 degrees. Collected the ether up to a temperature of 212 degrees. The product is a clear light brownish oil. Yields obtained 32 to 38 % of the theoretical.

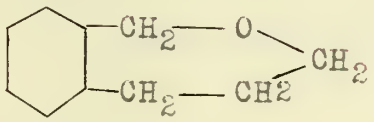
Specific gravity 1.0379 at 26° C.

Index of refraction 1.5046

Substance, 0.1437 gm. ; CO_2, 0.3790 gm. ; H_2O , 0.1098 gm.

Calc. for $C_{10}H_{14}O_2$	Found
C = 72.29%	C = 71.93%
H = 8.43%	H = 8.55%

2,3-benzo-trimethylene oxide



This compound is obtained from γ-hydroxy propyl benzyl ether by heating under a reflux condenser with its own weight of phosphorus pentoxide in toluene solution. Reflux for 2 hours.

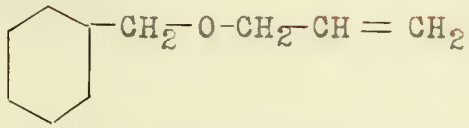
The toluene was distilled off first; finally, the ether under diminished pressure. The ether was collected at a temperature of 170 to 180 degrees at 40mm. On further distillation the allyl benzyl ether begins to come off at about 212 degrees. Yields of 68 to 78 % have been gotten.

Specific gravity	0.99647 at 26° C
Index of refraction	1.556

Substance, 0.1321 gm. ; CO_2, 0.3941 gm. ; H_2O, 0.0972 gm.

calc. for $C_{10}H_{12}O$	Found
C = 81.08%	C = 81.36 %
H = 8.10%	H = 8.22 %

Benzyl allyl ether



This compound is prepared by dissolving 1 mol of metallic sodium in 3 mols of benzyl alcohol at room temperature under a reflux condenser. One mol of allyl bromide is added to the sodium benzylate and the mixture refluxed for four hours. The solution is filtered and the excess alcohol is distilled off under a vacuum. The allyl benzyl ether is obtained as a clear yellow oil at a temperature of 198° C at 20 mm. Yields 28 to 35 %.

Specific gravity	1.0438 at 26° C
Index of refraction	1.551

Substance, 0.1880 gm. ; CO_2, 0.5572 gm. ; H_2O, 0.1304 gm.

Calc. for $C_{10}H_{12}O$	Found
C = 81.08 %	C = 80.8 %
H = 8.10 %	H = 7.77 %

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(2) Rindfusz, Jour. Amer. Chem. Soc., 41, 665, (1919)

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